# Development of a Reduced $C_3$ NEQAIR radiation model based on ab-initio calculations

Marat Kulakhmetov

Ph.D. Candidate at Purdue University

NASA Mentors:

Aaron Brandis

Brett Cruden

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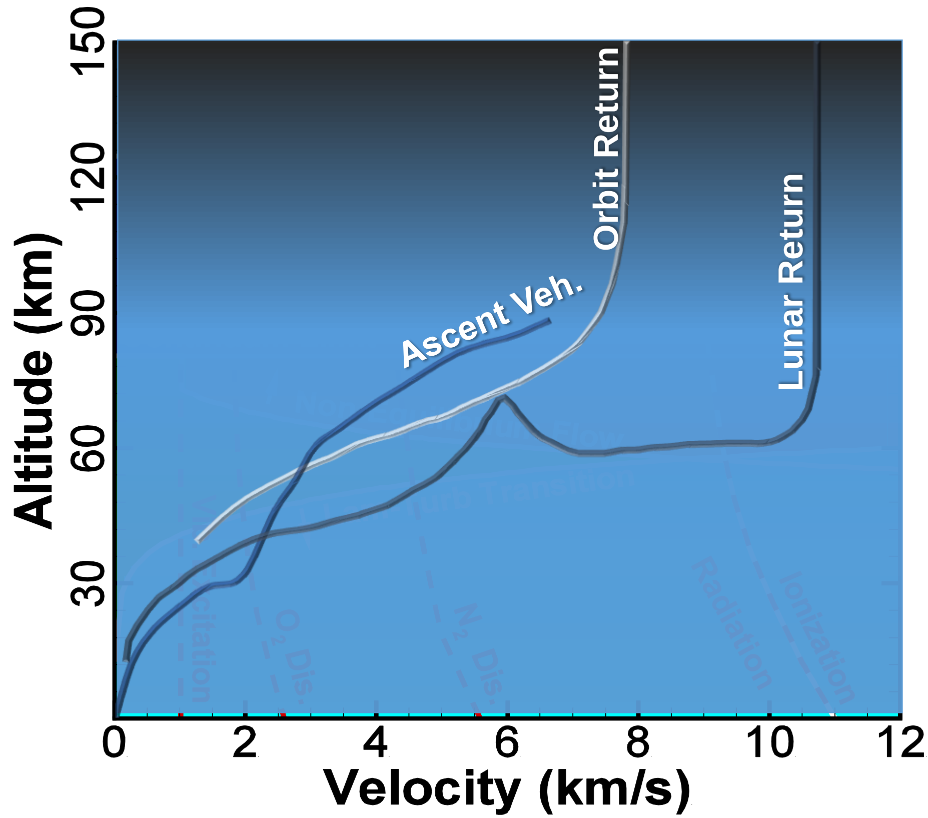
# Motivation

- Atmospheric entry spans a wide range of chemical physical regimes:
  - Laminar-Turbulent Transition
  - Thermo-Chemical Excitation
  - Continuum-Rarefied Transition
  - Nonequilibrium
  - Radiative transport



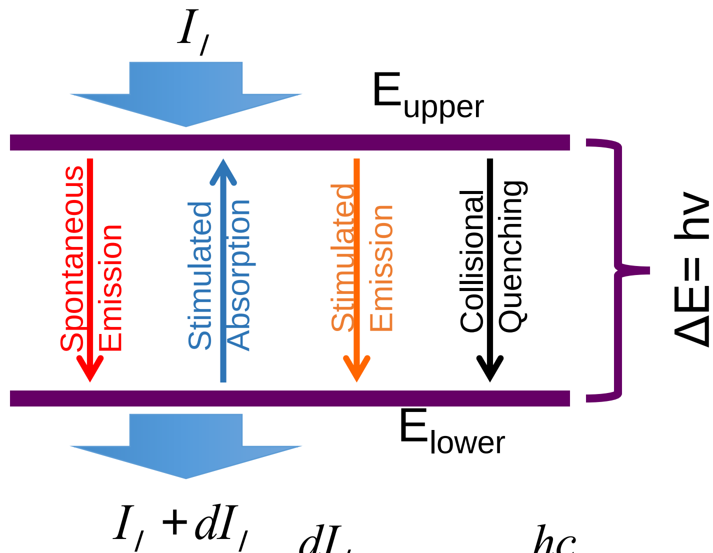

$L_{ref,1}$ = 5 m
$L_{ref,2}$ = 0.5 m

[1] M. Kulakhmetov, M. Gallis, A. Alexeenko, “Building a pathway between ab-initio quantum chemistry modeling and computational fluid dynamics,” Dynamics of Molecular Collisions, 2015

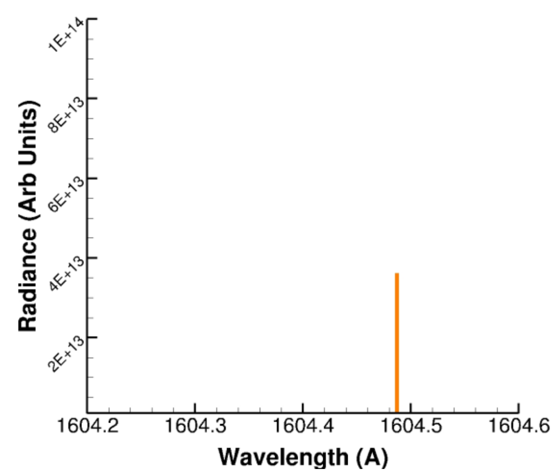
# Introduction

## Radiation

- Molecules may transition between internal energy levels by:
  - Spontaneous emissions
  - Stimulated Emissions
  - Stimulated Absorption
  - Collisions
- Radiance is a function of:
  - Transition wavelength
  - Einstein Coefficients
  - Population of levels -> f(g,N,T,E)
  - Broadening -> f(P,T)
- A full spectra is generated by considering
  - All energy levels
  - Allowed state to state transitions

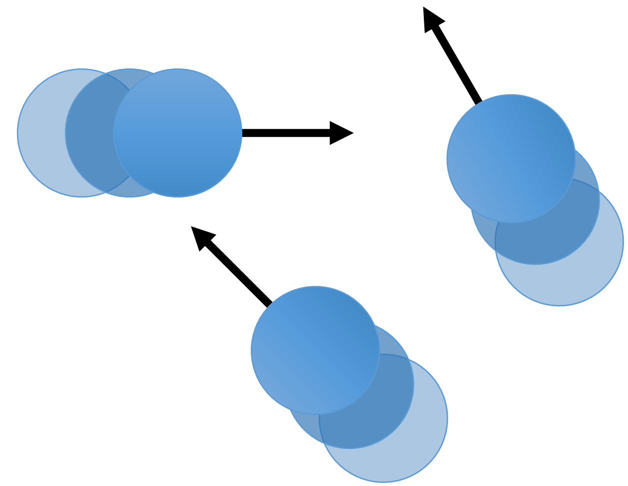



$$\frac{dI_\lambda}{dx} \sim E_\lambda \sim \frac{hc}{4\pi\lambda} A_{ul}$$



# Introduction

## Radiation



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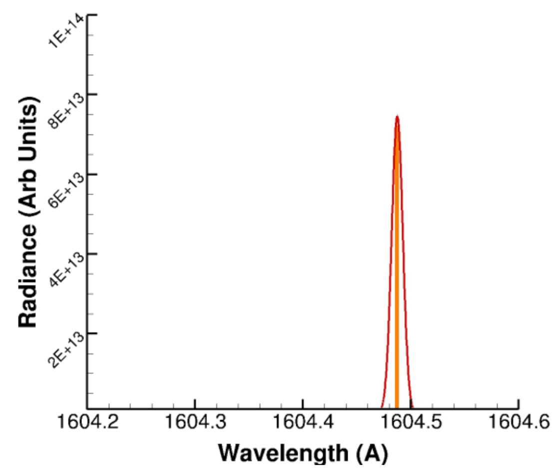
$$E_\lambda \sim \left[\frac{hc}{4\pi\lambda} A_{ul}\right] \underbrace{\left[g_u N \exp(-E_u/kT)/Q(T)\right]} \underbrace{\left[f_\lambda(P,T)\right]}$$



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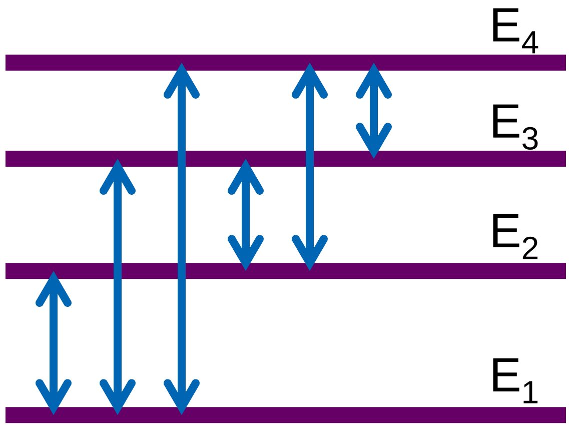
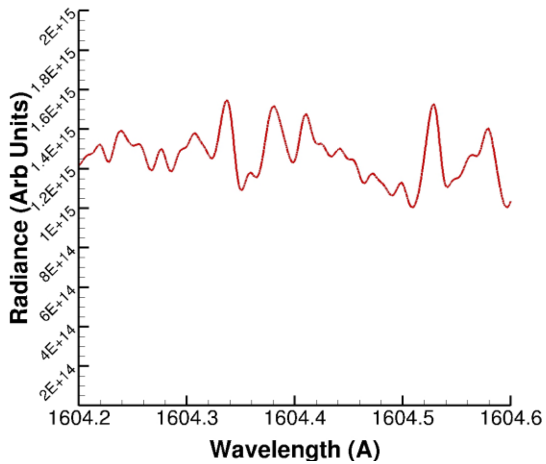
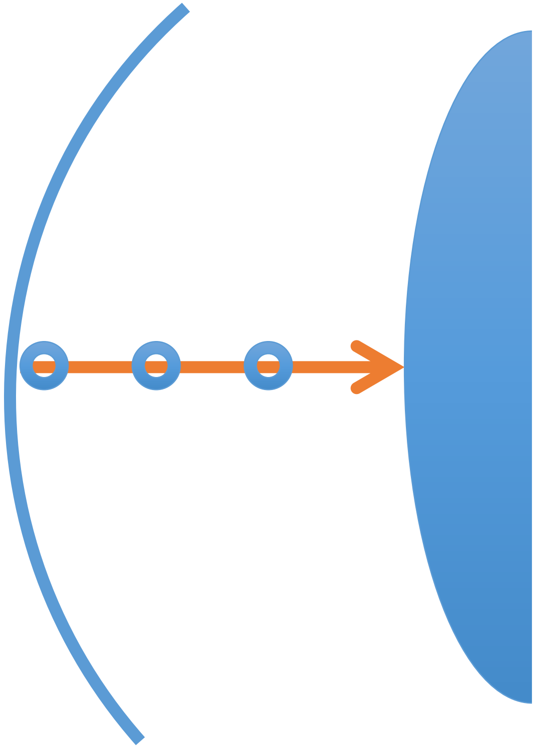



$$E_\lambda \sim \frac{Nhc}{4\pi Q(T)} \sum_{\lambda}^{\lambda+\Delta\lambda} \sum_{u\in\Delta\lambda} \frac{A_{ul}}{\lambda} g_u \exp(-E_u/kT)\phi_\lambda(P,T)$$





## NEQAIR

- Line-by-line line-of-sight code
- Calculates emission/absorption from a fluid media under thermo-chemical non-equilibrium conditions
- NASA Software of the Year?
- Is currently able to model emissions from:

| Molecular Bands | |
|---|---|
| N2 | NO |
| O2 | CN |
| CO | C3 |
| OH | H2 |
| NH | CH |
| CO2 | C3 |

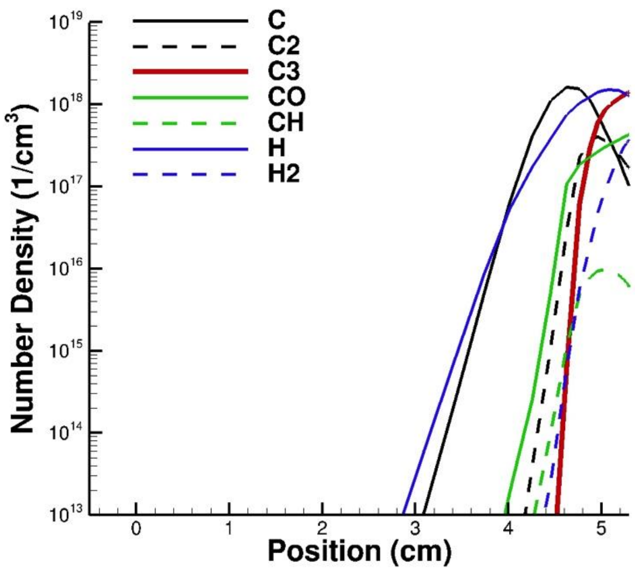
| Atomic Lines | |
|---|---|
| N | O |
| C | H |
| He | Ar |

$$\frac{dI_l}{dx} = E_l^{Spon.Emis} + \left(E_l^{Stim.Emis} - E_l^{Stim.Abs}\right) I$$

## What is $C_3$?

- Formed during vaporization of graphite/carbonaceous ablating heat

| Case | Dominant Boundary-Layer Species | Reference |
|---|---|---|
| Apollo Avcoat ablation | H, H2, C3, CO | [1] Park, et al, 2000 |
| Stardust peak heat flux | CO, C3, N2 | [2] Olynick et al, 1997 |
| 16-22 km/s carbon phenolic ablator | C,H,C3, CO, N2, N | [3] Johnston et al, 2015 |




- Is able to absorb in the 140-220 nm band
  - NO, Nitrogen and Oxygen atomic and molecular lines
  - ~60% of radiative heating in VUV

[1] C. Park, R. L. Jaffe, H. Patridge, “Chemical-Kinetic Parameters of Hyperbolic Earth Entry,” AIAA Journal, AIAA 00-0210
[2] D. R. Olynick, Y. K. Chen, M. E. Tauber, “Forebody TPS Sizing and Radiation and Ablation for the Stardust Sample Return Capsule, “ AIAA Paper 97-2474, June 1997
[3] C. O. Johnston, J. Samareh, A. M. Brandis, “Aerothermodynamic Characteristics of 16-22 km/s Earth Entry, AIAA Aviation, 2015

# Introduction

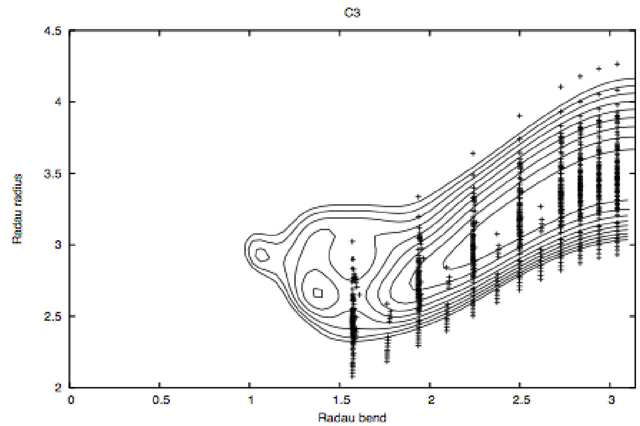
## Ab-initio Calculations

- $C_3$ potential surfaces have been calculated by R. Jaffe, G. Chaban and D. Schwenke using:
  - Complete Active Self-Consistent Field method (CASSCF) within the MOLPRO electronic structure package
  - Only available $C_3$ dataset
- Einstein coefficients can be calculated from a transition dipole moment,

$$M_{ul} = \int \psi_u^* \mu \psi_l \, d\tau$$

- As

$$A_{ul} = \frac{16\pi^3 \nu^3}{3\varepsilon_o h c^3} M_{ul}^3$$




$C_3$ X $^1\Sigma_g^+$ potential energy surface

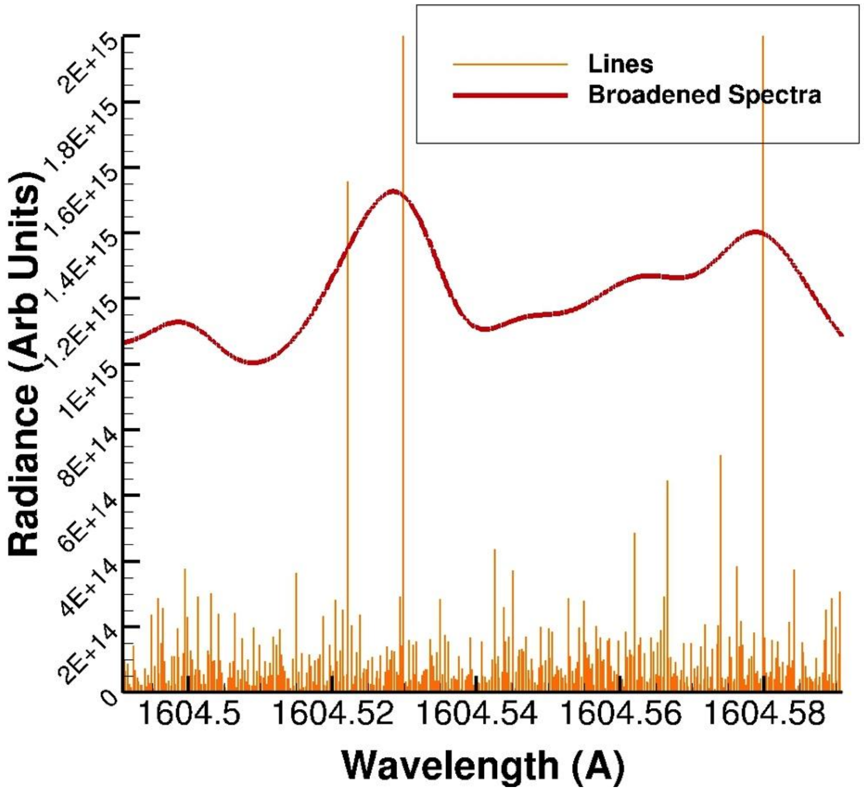
| Property | Value |
|---|---|
| Number of electronic levels | 19 |
| Number of rovibronic levels | ~ 745,000 |
| Number of lines | ~ 1.8 billion |
| Data size | >200 gigs |

[1] R. Jaffe, G. Chaban, D. Schwenke, “Theoretical Determination of High-Temperature Absorption Spectra for C3 in the near-UV and VUV”

# Reduced Radiation Model

## Selection of Strong Lines

- 1.8 billion lines need to be modeled efficiently within NEQAIR
- A complete set of lines are used to calculate an emission spectra, which depends on:
  - Strong lines
  - Density of weak lines
- Strong lines are selected by comparing to the local base of the spectra



# Reduced Radiation Model

## Fitting Weak Lines

- High density of weak lines can contribute significantly toward radiation.
- Combined emissivity and absorptivity of weak lines within λ+Δλ can be calculated as:

$$\varepsilon = \frac{hc}{4\pi\lambda}\,\frac{N}{Q(T)}\underbrace{\sum_{\lambda}^{\lambda+\Delta\lambda}\sum_{u\in\Delta\lambda} A_{ul}g_u \exp(-E_u/kT)}$$

$$\alpha = \frac{\lambda^4}{8\pi c}\,\frac{N}{Q(T)}\underbrace{\sum_{\lambda}^{\lambda+\Delta\lambda}\sum_{l\in\Delta\lambda} A_{ul}g_u \exp(-E_l/kT)} - \frac{\lambda^5}{2hc^2}\varepsilon$$

- These are fit to an exponential expansion to ensure better than 1% convergence in the 300-6,000 K temperature range

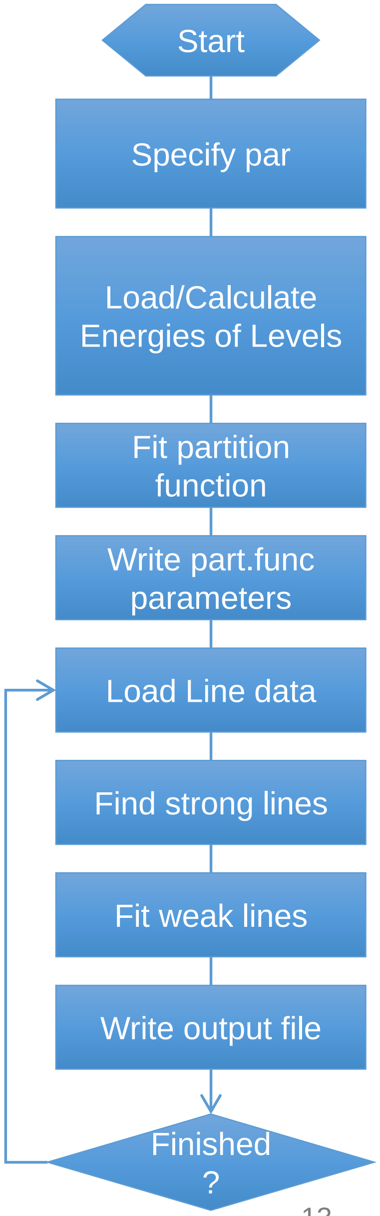
$$\underbrace{\sum_{\lambda}^{\lambda+\Delta\lambda}\sum_{u\in\Delta\lambda} A_{ul}g_u \exp(-E_u/kT)} = \sum_i A_i \exp(-B_i/T)$$

$$\underbrace{\sum_{\lambda}^{\lambda+\Delta\lambda}\sum_{l\in\Delta\lambda} A_{ul}g_u \exp(-E_l/kT)} = \sum_j C_j \exp(-D_j/T)$$

# Reduced Radiation Model

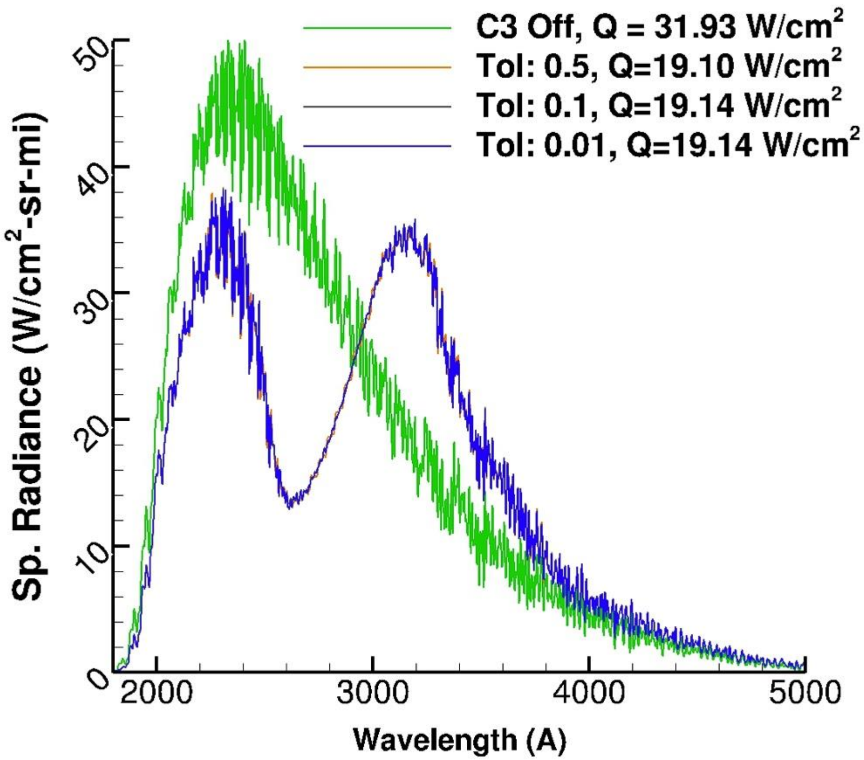
## SpectraRedux

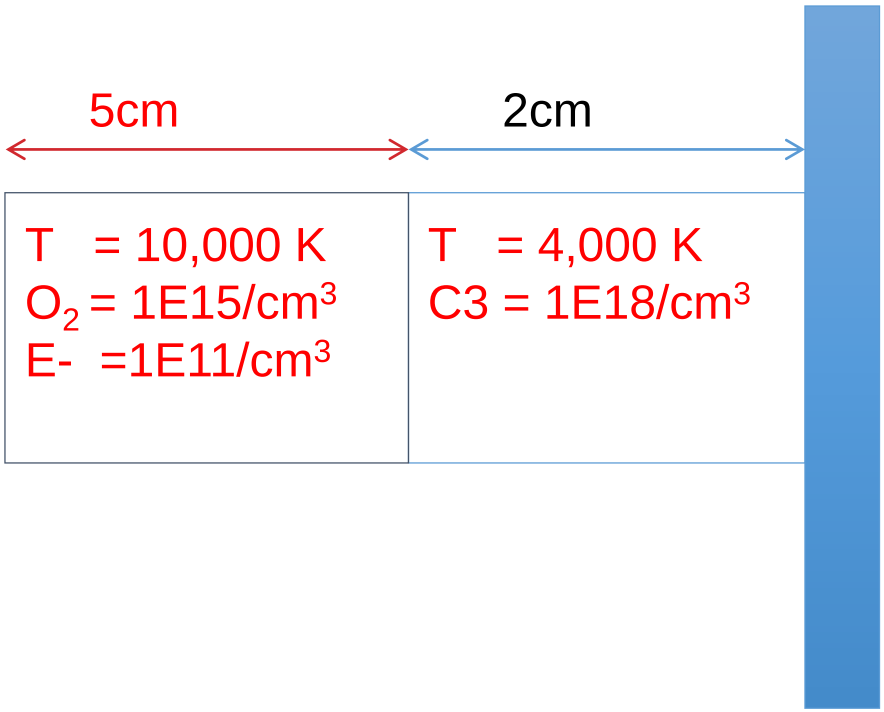
- A MATLAB program was created to produce Redux files for arbitrary ab-initio data that can be used by NEQAIR
  - User has to specify structure of the ab-initio output file
- The program is capable of producing 2-temperature models and can be extended to 4 temperature models
- C3 database reduction takes ~ 1 day on TSA cluster (in serial)
- NEQAIR 14.0 and 14.1 have been modified to accept C3 Redux files. – MPI compatible
  - Will be released as a feature in 14.1



# Results and Discussion

## 2-Cell Test Case



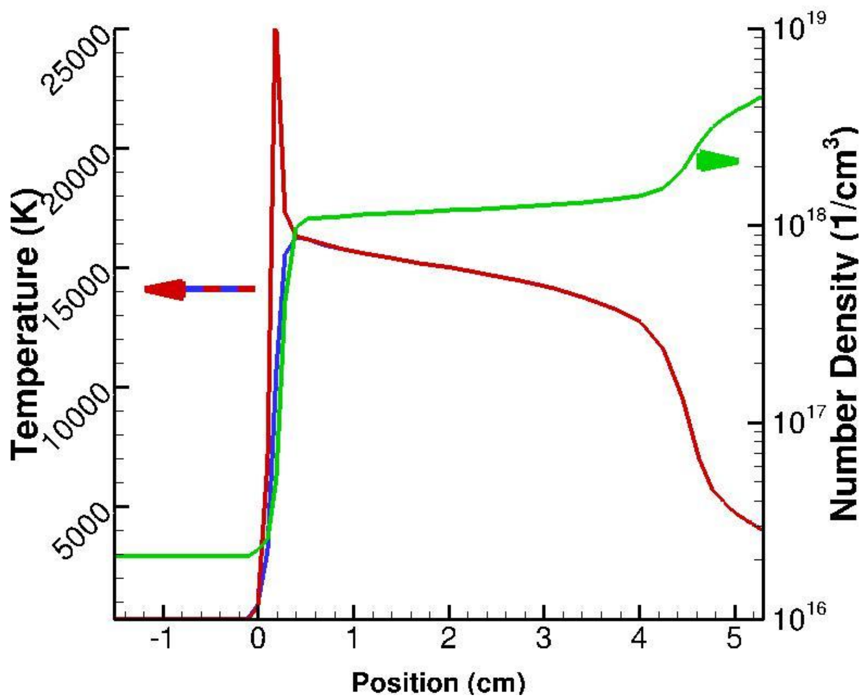



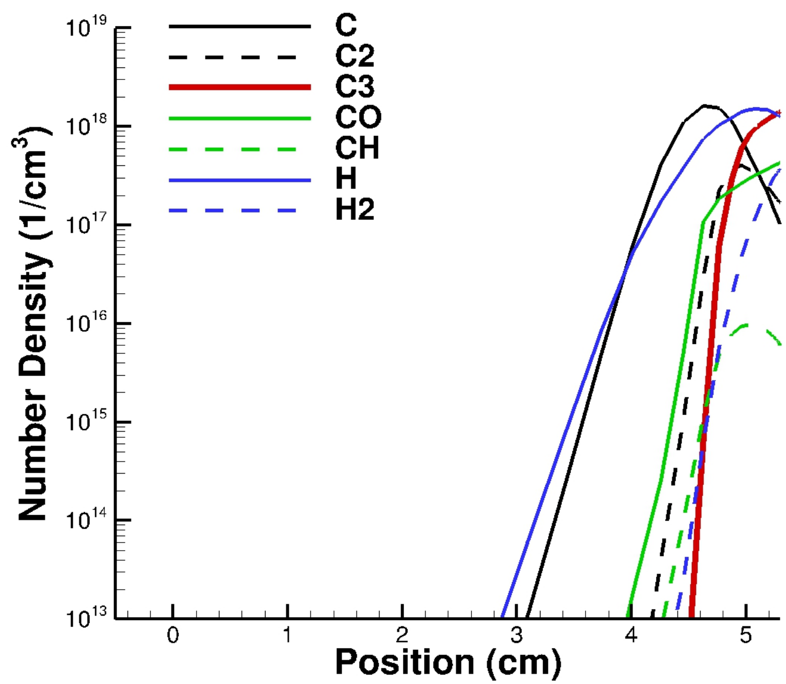

2-Cell test case is used for convergence studies:

- $C_3$ results in a 40% drop in heat flux
- Spectra is insensitive:
  - fit block width,
  - insensitive to Linecut tolerance parameter,

## Johnston Test Case

| Property | Value |
|---|---|
| Earth Entry | 16 km/s |
| Ablator: | Carbon Phenolic |
| Nose Radius | 1 m |
| Density | 1e-3 kg/m^3 |

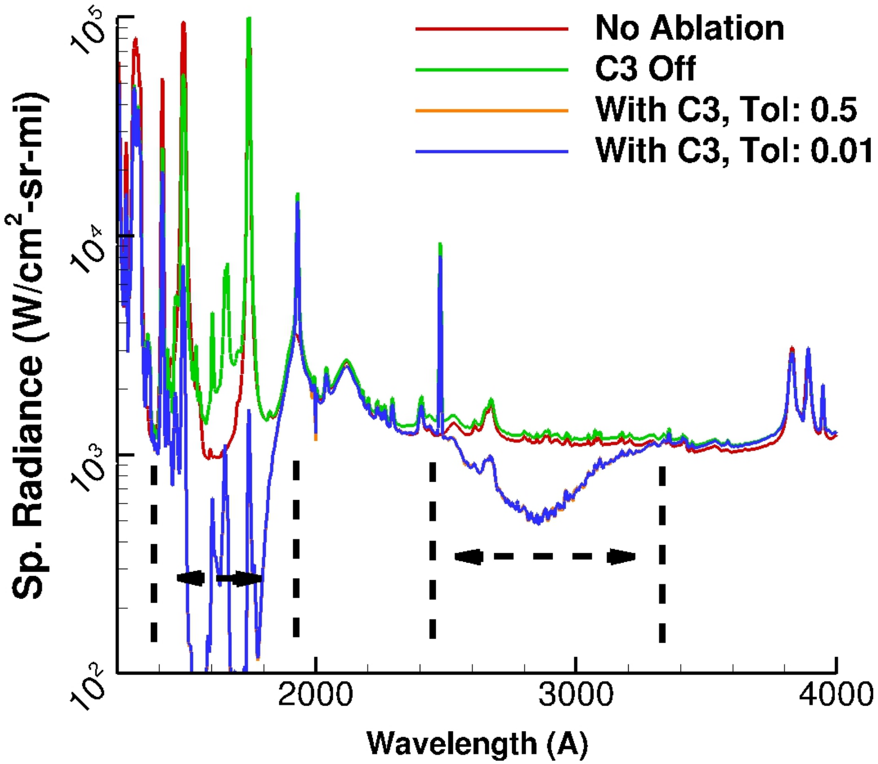



[1] C. O. Johnston, J. Samareh, A. M. Brandis, "Aerothermodynamic Characteristics of 16-22 km/s Earth Entry, AIAA Aviation, 2015

# Results and Discussion

## Johnston Test Case



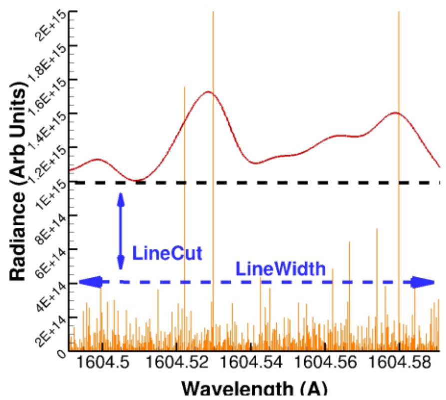

- Radiative heat transfer was calculated for Johnston's 16km/s flowfield
- Originally ablation resulted in 26.7% drop in heat flux
- Addition of C3 dropped heat flux by an additional 14.7%
  - weak lines absorb ~10% of radiation
  - Strong lines absorb ~5% of radiation
- C3 absorbs strongly in:
  - 140 nm - 180 nm
  - 240 nm – 320 nm

Johnston predicted:

- Non-Ablating: 1.60e4 W/cm2
- Ablating: 8.30e3 W/cm2 (23% diff)

# Results and Discussion

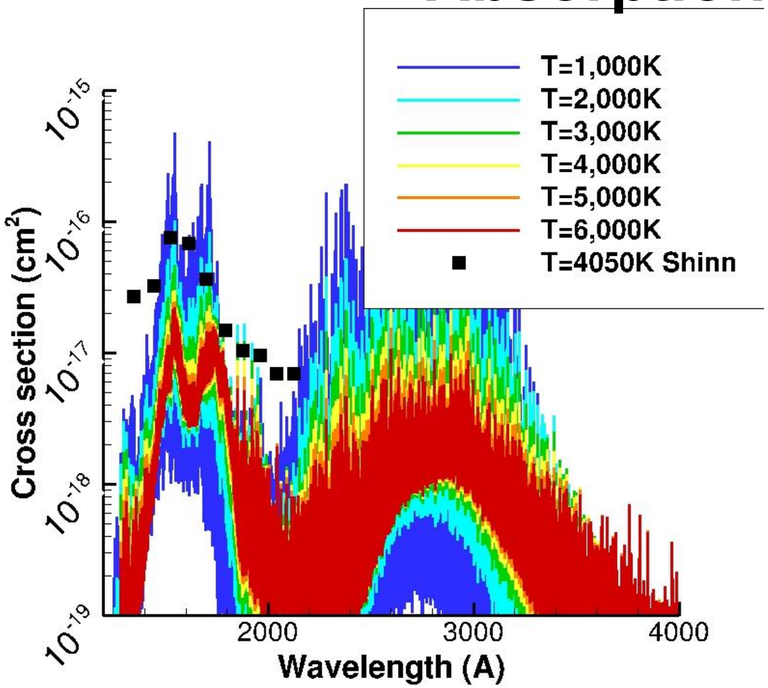
- Original file had:
  - 1,830,044,539 emission lines
  - 224 gigs of data
- Reduced C3 model
  - Kept: ½ - 2 million lines
  - ~ 1 - 30 % increase in computation time

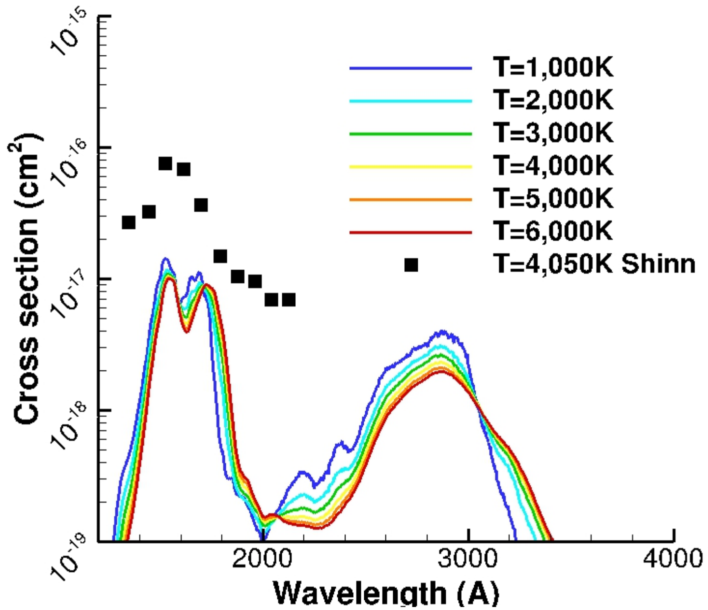



| Case | Heat Flux (W/cm^2) | % Change | # Lines | Size (MB) | Redux frac | Calc Time (s) | % Change |
|---|---|---|---|---|---|---|---|
| No Ablation | 17,280.68 | N/A | N/A | N/A | N/A | 323 | N/A |
| No C3 Radiation | 12,655.42 | 0.00% | N/A | N/A | N/A | 495 | 0.00% |
| LineCut: 0.5, Width: N/A, PreSort: 16G | 11,730.11 | 7.3 % | 552,203 | 27 | 8296 | 488 | -1.0% |
| LineCut: 0.5, Width: 5e2, PreSort: 16G | 10,861.15 | 14.2 % | 552,203 | 27 | 8296 | 498 | 0.60% |
| LineCut: 0.1, Width: 5e2, PreSort: 16G | 10,864.80 | 14.1 % | 1,760,732 | 86 | 2605 | 709 | 43.2% |
| LineCut: 0.1, Width: 5e2, PreSort: 90G | 10,797.39 | 14.7 % | 1,919,729 | 94 | 2383 | 654 | 32.1% |
| LineCut: 0.1, Width: 1e2, PreSort: 16G | 10,867.76 | 14.1 % | 1,866,664 | 91 | 2462 | 539* | 8.89% |
| LineCut: 0.01, Width : 5e2, PreSort: 16G | 10,867.91 | 14.1 % | 6,738581 | 328 | 683 | 786 | 58.8% |

# Results and Discussion

## Absorption Cross Section




- Ab-initio- calculated absorption cross sections are up to 1 order of magnitude lower than predicted by Shinn
  - Thermochemical equilibrium assumed
  - Thermodynamic data required for data reduction not accurately known
  - Possible contribution of other absorbing species
- $C_3$ emissions in HARA ( NASA Langley) are modeled using a polynomial fit of absorption cross sections based on data by Shinn
- Ab-initio data has been smoothed and fit with polynomial splines for implementation in HARA

[1] J.L Shinn, "Hydrocarbon Species from Shock Heated Acetylene and Methane in the 135-220 NM Wavelength Range," AIAA-81-1189

# Conclusions

- $C_3$ has been identified as an important absorber in ablating boundary layers
- Energy levels and Einstein coefficients for $C_3$ have been calculated by Jaffe, Chaban and Schwenke
- Ab-initio database for $C_3$ has been reduced and implemented in NEQAIR v14.0 and v14.1
- For a 16km/s test case, $C_3$ is able to absorb up to 14% of radiant energy reaching the surface.
- Calculated absorption cross sections are up to 1 order of magnitude lower than those previously measured by Shinn

- Deliverables
  - SpectraRedux code is able to reduce arbitrary ab-initio datasets
  - SpectraRedux manual
  - NEQAIR v14.0 and v14.1 is updated to accept the reduced $C_3$ model
    - Can be simply extended to other arbitrary molecules

# Questions?

National Aeronautics and
Space Administration

Ames Research Center
Entry Systems and Technology Division